Composition for the Fluorescent Whitening of Paper

The present invention relates to a composition for the fluorescent whitening of paper, the use thereof in either the pulp mass, in coating or in the metering size-press or film press and to a process thereto.

Traditional fluorescent whitening agents (FWA's) for paper, as disclosed, for example, in DE OS 2,715,864, are derivatives of 4,4'-bis[(1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid in which the triazine rings are substituted with anilino residues. Depending upon the requirements as to water-solubility and/or affinity, these anilino residues may be unsubstituted or substituted by one or two sulphonic acid groups, the resulting FWA's thus being designated as di-, tetra- or hexa-sulphonic acid derivatives.

However, in certain paper applications, in particular, in the metering size-press or film press, such conventional FWA's are disadvantageous since they either exhibit insufficient affinity (e.g. hexa-sulpho) or show low whitening effects and low saturation points (e.g. di-sulpho).

It is an object of the present invention to provide compositions, which show both high affinity to the paper and, at the same time, are highly effective in whitening with high saturation points.

Accordingly, the present invention relates to a composition for the fluorescent whitening of paper comprising

a) a fluorescent whitening agent derived from 4,4'-bis[(1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonic acid and characterized by one or both of the triazine rings carrying an $-NH_2$ substituent;
b) water and
c) optionally, further auxiliaries.

These compositions generally comprise

5 to 50% by weight of the FWA component a),

50 to 95% by weight of water and

0 to 40% by weight of component c), each range being based on the total weight of the composition and wherein the sum of the components a) to c) amounts to 100%.

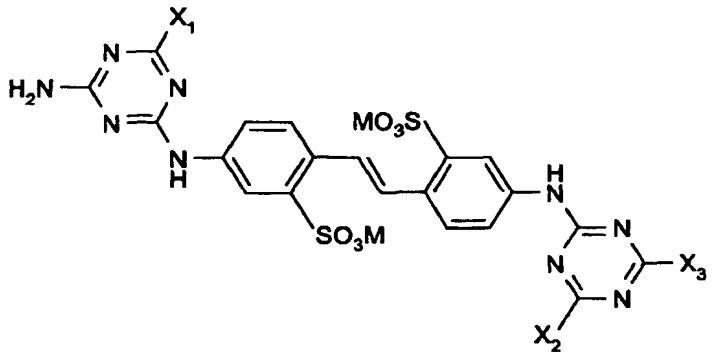
Preferably, however, these compositions are free flowing liquids and comprise

10 to 30%, especially 15 to 25% by weight of component a),

70 to 90%, especially 75 to 85%, by weight of water and

0 to 10% by weight of component c), or 0 to 40% in case polyethylene glycol is used as component c), each range being based on the total weight of the composition and wherein the sum of the components a) to c) amounts to 100%.

Component a) of the compositions, the fluorescent whitening agent, is a compound of the formula I



(I)

wherein

X_1, X_2 and X_3 each, independent of the other, represent $-NR_1R_2$ or $-OR_3$, wherein

R_1 and R_2 are, independently of each other, hydrogen, a C_1-C_4alkyl-group, which is unsubstituted or substituted by one or two of the following residues selected from the group consisting of C_1-C_4alkoxy, hydroxy, carboxy, cyano, carbonamido, thiol, guanidine, substituted or unsubstituted phenyl, unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkyl, halogen, a heterocycle and a sulphonic acid residue, and wherein the carbon chain of an alkyl group having two, three or four carbon atoms can be interrupted by oxygen,

or, alternatively,

R_1 and R_2, together with the nitrogen atom linking them, complete a 5- or 6-membered heterocyclic ring;

R_3 represents C_1-C_4alkyl and

M represents H, Na, Li, K, Ca, Mg, ammonium, or ammonium that is mono-, di-, tri- or tetra-substituted by C_1-C_4alkyl and/or C_2-C_4hydroxyalkyl.

Preferably, however, component a) is a compound of formula (1), in which

X_1 and X_2 each independently, represent $-NH_2$, $-NHC_1$-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$,

-NHC_2-C_4hydroxyalkyl, -$N(C_2$-C_4hydroxyalkyl$)_2$, -$N(C_1$-C_4alkyl$)(C_2$-C_4hydroxyalkyl), -$NH(C_2$-C_4alkylene-C_1-C_4alkoxy), -$N(C_2$-C_4alkylene-C_1-C_4alkoxy$)_2$, -NHC_1-C_4alkylphenyl, tetrahydrofurfurylamino, morpholino, piperidino, pyrrolidino or cyclohexylamino or an amino acid or amino acid amide residue from which a hydrogen atom has been abstracted from the amino group and

X_3 represents -NH_2,

M being as previously defined.

Most preferable compositions are those in which, in the compound of formula (1),

X_1 and X_2 both represent -NH_2, -NHC_1-C_2alkyl, -$N(C_1$-C_2alkyl$)_2$, -$NHCH_2CH_2OH$, -$N(CH_2CH_2OH)_2$, -$N(C_1$-C_2alkyl$)(CH_2CH_2OH)$, -$NHCH_2CH_2OCH_3$, -$N(CH_2CH_2OCH_3)_2$, -$NHCH_2CH_2$-O-CH_2CH_2-OH, -$N(CH_2CH_2$-O-CH_2CH_2-OH$)_2$, -$NHCH_2CO_2$M", -$N(CH_3)CH_2CO_2$M", -$NHCH_2CH_2CO_2$M", -$NHCH(CO_2$M"$)CH_2CH_2CH_2NHC(=NH)NH_2$, tetrahydrofurfurylamino, benzylamino, cyclohexylamino, pyrrolidino or morpholino,

X_3 represents -NH_2 and

M" represents H, K, Na, ammonium or ammonium that is mono-, di-, tri- or tetra-substituted by C_1-C_4alkyl and/or C_2-C_4hydroxyalkyl, especially Na.

Within the scope of the definitions of the substituents, C_1-C_4alkyl groups are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl or t-butyl, whilst C_1-C_4alkoxy groups are, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-, sec-, iso- or t-butoxy. A C_2-C_4alkylene chain, may, for example be an ethylene, n-propylene, methyl ethylene, 1- or 2-methylpropylene, n-butylene or ethylethylene residue, whilst C_2-C_4 hydroxyalkyl may be 2-hydroxyethyl, 2- or 3-hydroxy-n- or isopropyl or hydroxybutyl.

Further, within the scope of the definitions, halogen is iodine, bromine, chlorine, fluorine or, especially, chlorine, whilst C_5-C_7cycloalkylamino is cyclopentylamino, cyclohexylamino, cycloheptylamino or, especially, cyclohexylamino.

A carbonamido group may be –C(=O)NH C_1-C_4alkyl, -C(=O)$N(C_1$-C_4alkyl$)_2$ or, especially, -$C(=O)NH_2$.

A heterocyclic residue may be a five-, six- or seven-membered ring having one or two heteroatoms such as oxygen, sulfur or nitrogen, the rest of the skeleton being carbon atoms.

Examples are 2- or 3-tetrahydrofurfuryl, 2- or 3-furyl, 2- or 3-thienyl, 2- or 3-pyrrolyl, 2-, 4- or 5-imidazolyl, 2-, 3- or 4-pyridyl, pyrazinyl, 3-isothiazolyl, 3-isoxazolyl or 2- or 3-pyrrolidinyl.

An amino acid or amino acid amide residue from which a hydrogen atom has been removed may be derived from glycine, alanine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β-indolylalanine), histidine ((β-imidazolylalanine), α-aminobutyric acid, methionine, valine (α-aminoisovaleric acid), norvaline, leucine (α-aminoisocaproic acid), isoleucine (α-amino-β-methylvaleric acid), norleucine (α-amino-n-caproic acid), arginine, ornithine (α,δ-diaminovaleric acid), lysine (α,ε-diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α-aminoglutaric acid), threonine, hydroxyglutamic acid and taurine, as well as mixtures and optical isomers thereof.

A further preferred example of an aminoacid from which an aminoacid residue R_1 may be derived is iminodiacetic acid or the mono- or diacid amide thereof, whilst a suitable amino acid amide is 2-hydroxyethylaminopropionamide.

Suitable optional auxiliaries of the composition, component c), include, for example, anionic or non-ionic dispersants from the class of ethylene oxide adducts with fatty alcohols, higher fatty acids or alkyl phenols or ethylenediamine ethylene oxide-propylene oxide adducts, copolymers of N-vinylpyrrolidone with 3-vinylpropionic acid, polyethylene glycols having an average molecular weight of from 300 to 10,000, water retention aids, including glycols such as ethylene glycol, glycerol or sorbitol, or biocides or further auxiliaries such as urea, lactones or lactams such as N-methyl pyrrolidone, and other solubilizing agents such as dimethyl formamide or dimethyl sulphoxide.

The present invention further provides a process for the fluorescent whitening of paper or paperboard comprising contacting the substrate with the fluorescent whitening agent composition of the invention.

When used for the fluorescent whitening of paper, the composition of the invention may be applied to the paper substrate in the pulp mass, in the form of a paper coating composition, or directly in the metering size press or film press.

A further aspect of the present invention provides use of the composition of the invention in a process for the fluorescent whitening of a paper surface, comprising contacting the paper surface with a coating composition comprising a white pigment; a binder dispersion; optionally a water-soluble co-binder; and a sufficient amount of a fluorescent whitening agent composition, according to the present invention, to ensure that the treated paper usually contains 0.01 to 1 % by weight, based on the white pigment, of a fluorescent whitening agent of formula (1).

As the white pigment component of the paper coating composition used according to the method of the present invention, there are preferred inorganic pigments, e.g., aluminium or magnesium silicates, such as China clay and kaolin and, further, barium sulfate, satin white, titanium dioxide, calcium carbonate (such as chalk, natural or precipitated calcium carbonate) or talcum; as well as white organic pigments.

The paper coating compositions used according to the method of the present invention may contain, as binder, inter alia, plastics dispersions based on copolymers of butadiene/styrene, acrylonitrile/butadiene/styrene, acrylic acid esters, acrylic acid esters/styrene/acrylonitrile, ethylene/vinyl chloride and ethylene/vinyl acetate; or homopolymers, such as polyvinyl chloride, polyvinylidene chloride, polyethylene and polyvinyl acetate or polyurethanes. A preferred binder consists of styrene/butyl acrylate or styrene/butadiene/ acrylic acid copolymers or styrene/butadiene rubbers. Other polymer lattices are described, for example, in the following US patents: 3,265,654, 3,657,174, 3,547,899 and 3,240,740.

The optional water-soluble protective colloid may be, e.g., soya protein, casein, carboxymethylcellulose, natural or modified starch, chitosan or a derivative thereof or, especially, polyvinyl alcohol. The preferred polyvinyl alcohol protective colloid component may have a wide range of saponification levels and molecular weights; e.g. a saponification level ranging from 40 to 100; and an average molecular weight ranging from 10,000 to 100,000 g/mol.

Recipes for coating compositions for paper are described, for example, in J.P. Casey "Pulp and Paper"; Chemistry and Chemical Technology, 2nd edition,

Volume III, pages 1684-1649 and in "Pulp and Paper Manufacture", 2nd and 5th edition, Volume II, page 497 (McGraw-Hill).

The paper coating compositions used according to the method of the present invention preferably contain 1 to 65% by weight of a white pigment. The binder is preferably used in an amount, which is sufficient to make the dry content of polymeric compound up to 1 to 30% by weight, preferably 3 to 25% by weight, of the white pigment. The amount of fluorescent brightener preparation used according to the invention is calculated so that the fluorescent brightener is preferably present in amounts of 0.01 to 2% by weight, more preferably 0.05 to 1% by weight, and especially 0.05 to 0.6% by weight, based on the white pigment.

The paper coating composition used in the method according to the invention can be prepared by mixing the components in any desired sequence at temperatures from 10 to 100°C, preferably 20 to 80°C. The components here also include the customary auxiliaries such as binders, co-binders, rheological modifiers, water retention auxiliaries, dispersants, wet strength agents and boosters. Such auxiliaries are, for example, natural binders, such as starch, casein, protein or gelatin, cellulose ethers, such as carboxyalkylcellulose or hydroxyalkylcellulose, alginic acid, alginates, polyethylene oxide or polyethylene oxide alkyl ethers, copolymers of ethylene oxide and propylene oxide, polyvinyl alcohol, water-soluble condensation products of formaldehyde with urea or melamine, polyphosphates or polyacrylic acid salts.

The coating composition used according to the method of the present invention is preferably used to produce coated printed or writing paper, or special papers such as ink-jet or photographic papers, or cardboard.

The coating composition used according to the method of the invention can be applied to the substrate by any conventional process, for example with an air blade, a coating blade, a roller, a doctor blade or a rod, in the size press, a metering size press, or by spraying, after which the coatings are dried at a temperature in the range from 70 to 200°C, preferably 90 to 130°C, to a residual moisture content of 3 to 8%, for example with infra-red driers and/or hot-air driers.

Comparably high degrees of whiteness are thus achieved even at low drying temperatures.

In another preferred aspect, the present invention provides a method for the fluorescent whitening of a paper surface comprising contacting the paper in the size press or metering size press with an aqueous solution containing a size, optionally an inorganic or organic pigment and 0.1 to 20 g/l of a fluorescent whitening agent composition of the invention. Preferably, the size is starch, a starch derivative or a synthetic sizing agent, especially a water-soluble copolymer or mixtures thereof.

In a further preferred aspect, the invention provides a method for the fluorescent whitening of paper during paper formation, whereby the FWA composition is added directly to the pulp mass. In this case, the FWA composition may be in the form of a solution or a dispersion, whereby the FWA compositions of the invention are especially valuable in that their effect is only slightly inhibited by the presence of cationic polymers, fixing agents, wet-strengthening agents or de-inking auxiliaries, which are similarly added to the pulp mass prior to paper formation. Examples of such auxiliaries may include dicyandiamide condensation products, polyvinyl amines, polyethylene imines, cationic starches, poly-DADMAC (diallyl dimethyl ammonium chloride), polyamide amines and polyepoxides.

Another embodiment of the present invention relates to paper, which has been treated with a fluorescent whitening agent composition according to the invention.

The compositions of the invention may be obtained by mechanical mixing of the individual components a), b) and, optionally, c) at ambient or elevated temperature until homogenous solutions or dispersions are obtained.

The fluorescent whitening agents, components a), of the invention are known compounds or may be obtained in analogy to known methods as described, for example, in GB 1,183,854.

The compositions of the present invention are particularly advantageous in that they exhibit not only extremely high whitening ability, but, in addition, in many cases highly desirable water solubilities and fastness properties.

By the use of the method according to the invention, the coatings obtained are distinguished by optimum distribution of the fluorescent brightener over the entire surface and by an increase in the level of whiteness thereby achieved, by a high fastness to light and to elevated temperature (e.g. stability for 24 hours at 60 to 100°C) and excellent bleed-fastness to water.

The following Examples serve to illustrate the invention without intending to be restrictive in nature; parts and percentages are by weight, unless otherwise stated.

Examples

Examples 1-19

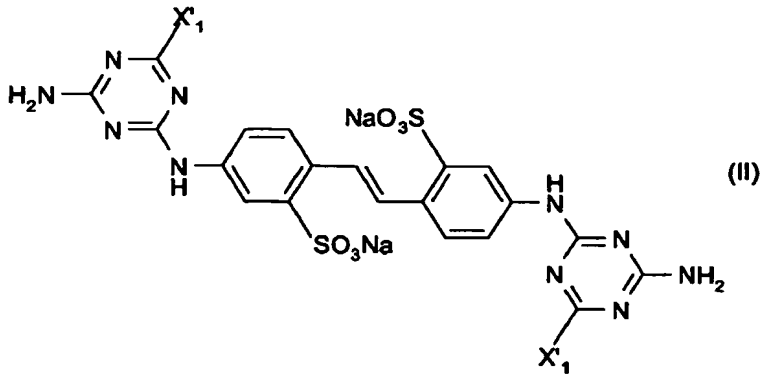
Size-press Application

To an 8% by weight solution of a commercially available partially degraded anionic starch (Perfectamyl® A 4692; Avebe company) is added sufficient of an aqueous FWA solution or dispersion to result in solutions having final concentrations of 3g/kg and of 6g/kg of FWA respectively.

The resulting composition is then applied in a size-press to a neutral-sized, wood- and FWA-free paper having a basis weight of 80g/m^2 with an uptake of 20% of the composition, based on the weight of the paper.

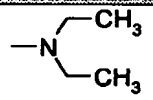
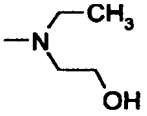
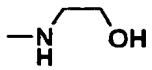
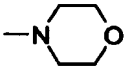
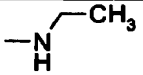
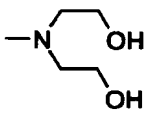
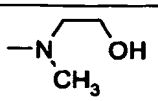
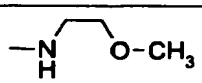
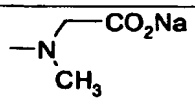
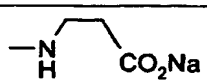
The degrees of whiteness, Wcie, are then measured using a Datacolor Elrepho 3000 spectrophotometer.

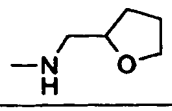
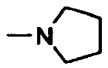
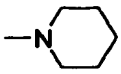
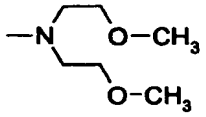
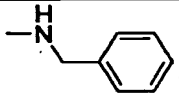
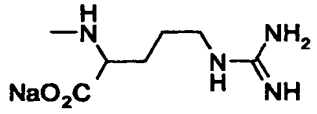
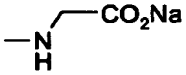
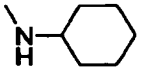
The results are summarized in the following Table 1, wherein the FWA's are of formula (II):



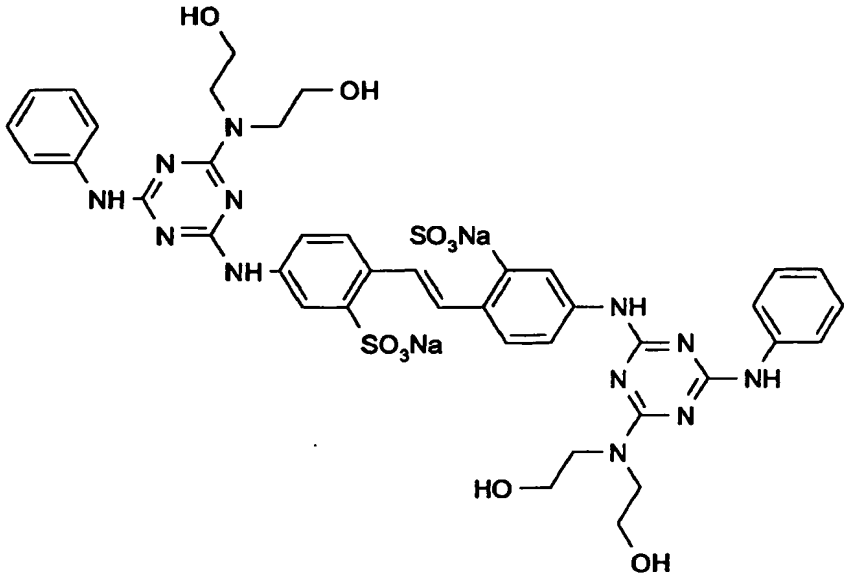
(II)

Table 1

Example Nr.	X'_1	Wcie (3g/kg)	Wcie (6g/kg)
1		120	109
2		120	124
3		120	124
4	$-NH_2$	120	125
5		119	124
6		119	126
7		119	124
8		119	126
9		118	125
10		118	125
11		117	127

12		117	124
13		117	120
14		115	123
15		115	124
16		115	121
17		114	119
18		107	116
19		105	110

In comparison to the compositions of the invention, the corresponding values, Wcie, for the conventional FWA, of the formula



are 109 and 110, respectively, thus demonstrating significant improvement in both saturation point and degree of whiteness of the majority of the instant compositions.